CHEMICALS HAZARD MANAGEMENT AT EXXONMOBIL

JOINT DOE/EFCOG

CHEMICAL MANAGEMENT 2001 WORKSHOP

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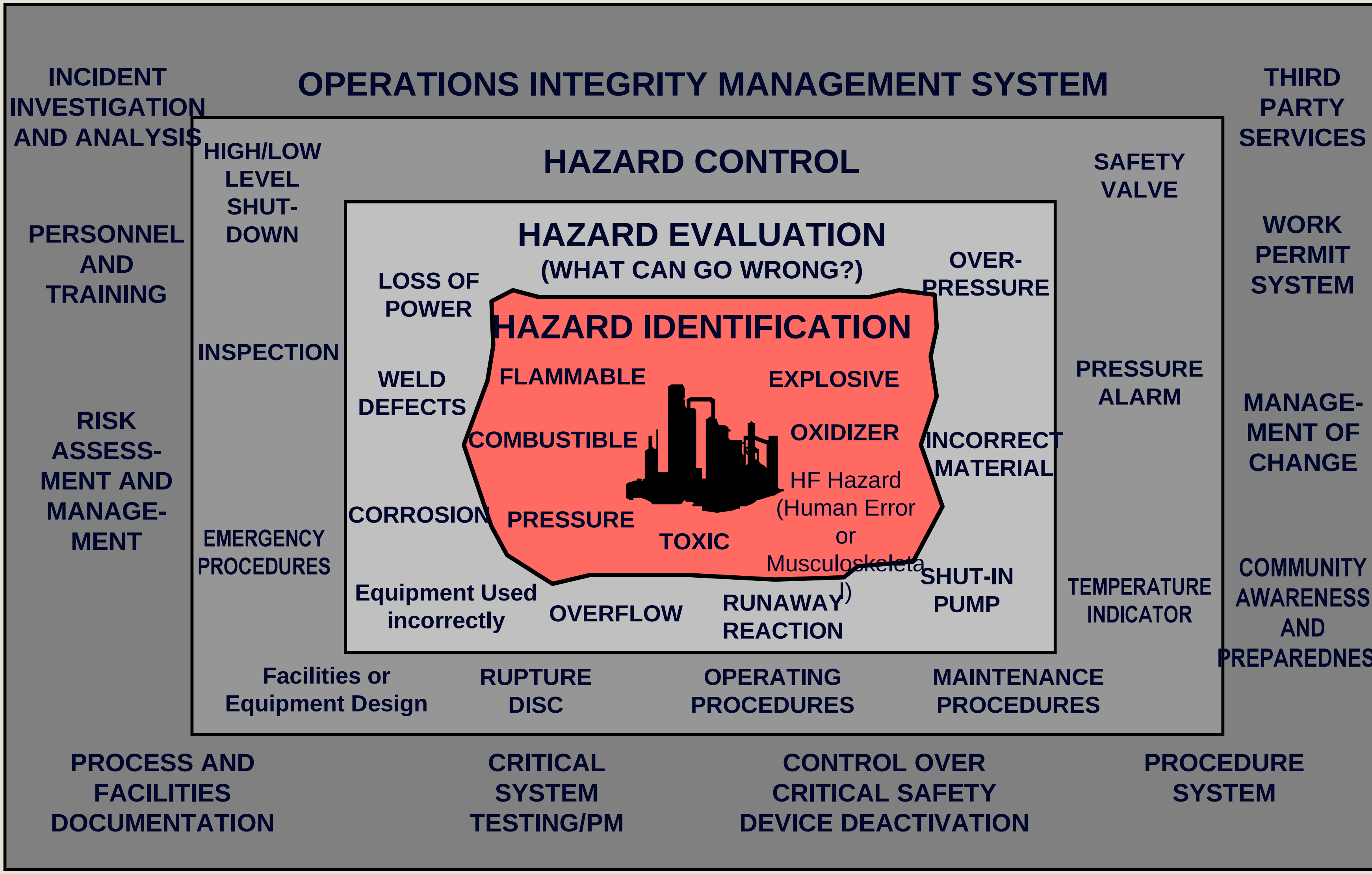
October 23, 2001

Chemicals Hazard Management at ExxonMobil

- Comprehensive process in all facets of operations, and in capital project development and implementation
- Existing operations required to conduct specific SHE analyses on a periodic basis
  - HAZOP -- Review P&ID's, identify and evaluate potential hazards and operability problems
  - Risk Reassessment -- Identify highest level risk scenarios and assess adequacy of controls in place
  - Safety Relief Design Review -- Examine capability of pressure relief and blowdown facilities to handle design and emergency contingencies
  - Exposure Assessment Strategy -- Review health hazards and controls for potentially hazardous tasks
  - Also Task Risk Analysis, Environmental Assessments, Security Risk Assessments

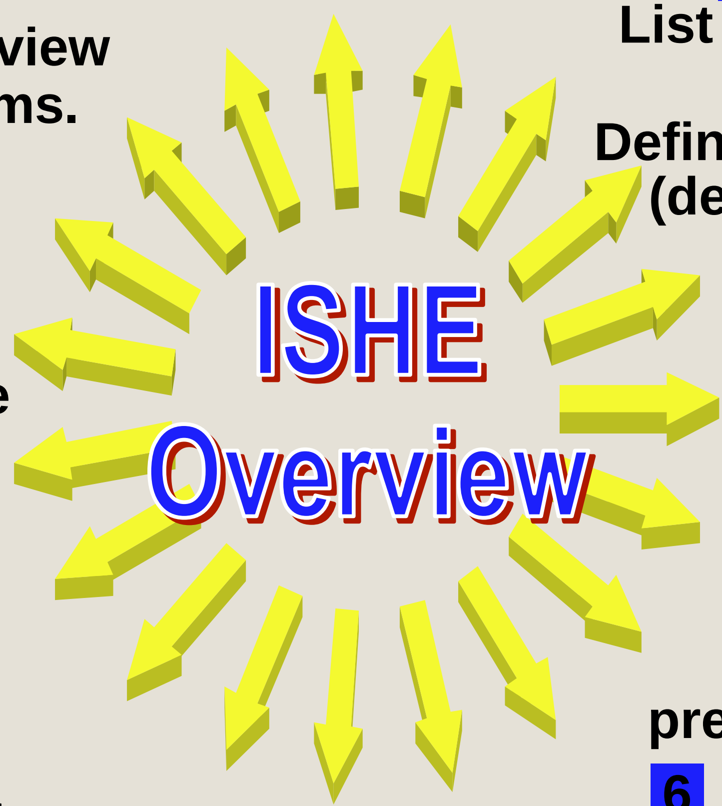
Hazard Management Process



Managing Chemical Hazards in Capital Project Development

- Project Execution Procedures define explicit requirements and associated timing
- HAZOPs and Non-Process Quality Control are primary procedures
- Reliance on Inherent SHE principles
  - Primary objectives are to reduce or eliminate hazards and to minimize the need to manage safety critical equipment or procedures
- Inherent SHE Reviews conducted
  - During the Research and Development phase
  - During DBM (Design Basis Memorandum) preparation
  - During the PDS (Process Design Spec) HAZOP Review
  - After plant start-up

ISHE Process Overview



1 Prepare simplified process flow diagram.

2 List all chemicals.

3 Define chemical reactions (desired & undesired).

4 Define physical, chemical & toxic properties.

5 Define process pressure & temperature conditions.

6 Estimate quantities used in each process system.

7 Define site specific issues.

8 Define major potential hazards.

9 Identify potential HF Design Issues

10 Review each process and hazardous material for ways to improve Inherent SHE.

11 Document review & action items.

ISHE Review ‘Triggers’

– Are Major Hazard (Consequence Category) thresholds exceeded?
– Are Hazardous Material trigger quantities exceeded?
– Are tasks envisaged that may require Critical Task Analysis?

A definite “No” to these questions is required to waive the ISHER.

- “Don’t know yet” is treated as “Yes”

Prior to the

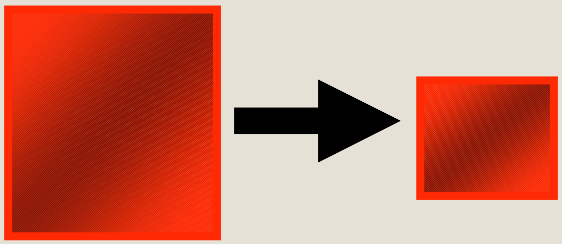
- Establish Design Basis (plant capacity)
- Simplified Process Flow Diagram
- Define Chemical Reactions
- Obtain Runaway Reaction and Decomposition Data
- List all Chemicals and their Properties
- Define Health/Environmental Hazards
- Identify Critical Operator Duties, for example: Reactor catalyst replacement or filter replacement
- Define Site and Environmental Permitting Issues
- Define Compatibility Problems
- Define Process Conditions (T&P)
- Estimate Quantities of:
  - Raw materials
  - Intermediates/Products
  - Wastes and Emissions

Define Physical and Toxic Properties

Many of these properties can be found on an MSDS

- **Composition (Normal, Minimum, and Maximum) Physical Data**
  - State at Ambient
  - Melting Point
  - Boiling Point
  - Vapor Pressure Curve
  - Vapor Density (MW)
  - Water Solubility
- **Flammable Data**
  - Flash Point
  - Flammability Range
  - Autoignition Temperature
  - Detonable
  - Pyrophoric
  - NFPA Rating
- **Chemical Reactivity Data**
  - Reactions with other materials (water, air, etc.)
  - NFPA Rating
- **Acute Toxicity**
  - Describes Exposure Limits
- **Chronic Toxicity**
  - Describes Exposure Limits & Effects
- **Odor Threshold**
- **Ozone Depletion Potential**

INTENSIFY



Prevent large leaks by reducing inventories and reaction volumes while preserving or improving throughput

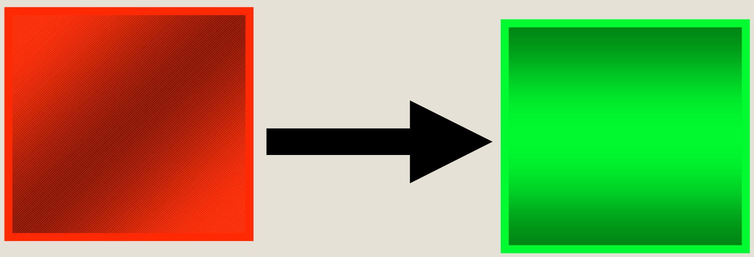
– Small continuous vs. large batch processing
– Rate of reaction vs. mixing
– Use less, little, or no intermediate storage
– Reduce hold-up, equipment inventory

P A Y O F F

Unit is downsized - less hazard, removes from continual re-evaluation of risk

SUBSTITUTE

Use a less hazardous material



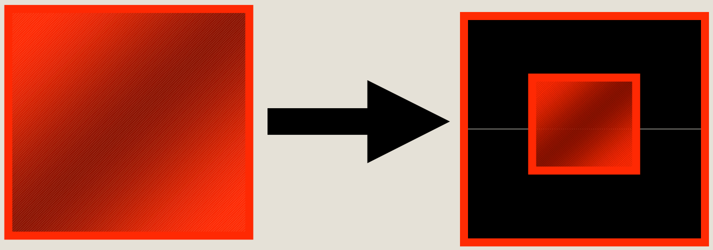
– Less toxic or non toxic
– Nonflammables or combustibles versus flammables
– New chemistry

P A Y O F F

Cheaper plants due to less protective equipment which are also safer plants

ATTENUATE

Process a hazardous material under less hazardous conditions

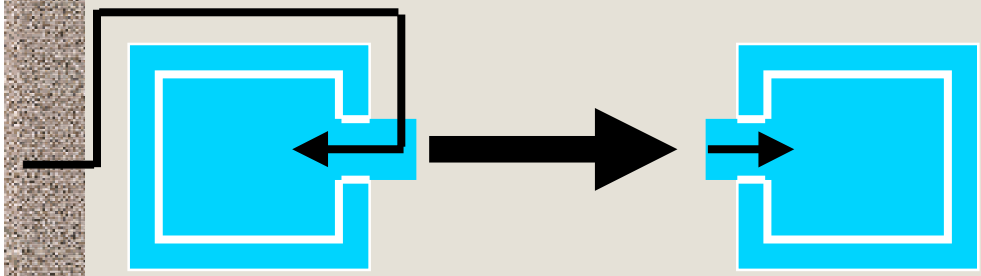


- Lower pressure or temperature
- Choose least hazardous phase (vapor, liquid or solid)
- Diluted with safe solvent

P A Y O F F

Less protective equipment needed

SIMPLIFY



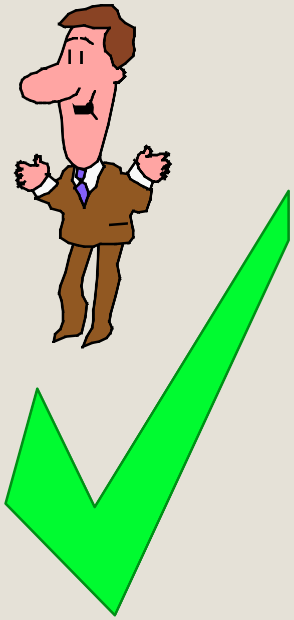
Complicated plants are expensive and provide many opportunities for error

- Flexibility/integration vs ease of operation
- Presentation of information
- Abnormal process situations
- Recognition of human capability

P A Y O F F

Recognize hazards in the design process early to avoid them by design change instead of adding protective equipment

Inherent SHE Successes



- Inventories of toxic materials were reduced by over 100 tons from Risk Assessments after Bhopal
- Solid chemicals are being used in some locations to treat cooling tower water rather than chlorine
- Pressurized "light ends" sphere storage reduced by over 50% (Eliminated four spheres)
- Leakless valves and pumps, low NOx burners, have reduced permitting and monitoring costs
- Reduced inventory of HCL from one 23,000 lb tube trailer to two 600 lb cylinders; HCL is no longer a toxic threat beyond property line
- During project development, a reactor was changed to a shell and tube pumparound design that was inherently safer
- On a capital expansion, ISHE concepts resulted in eliminating a number of pumps, tanks, and other equipment

What is Reactive Chemistry?

- Recognition and understanding of incipient runaway conditions due to uncontrolled chemical reaction
- Quantification of the consequences of potential runaway events
  - Heat and/or gas generation leading to temperature and/or pressure build-up
  - Equipment capability to dissipate excessive temperature and pressure
- When is a reactive chemistry study warranted?
  - New process development with new chemistry
  - Pushing existing processes to new conditions
  - Occurrence of an incident or a near miss
  - Feed changes, catalyst changes, possibility of impurities
  - Presence of highly active molecular bonds
  - New design or new equipment

Reactive Chemical Screening

- Define desired reactions and associated thermodynamics
  - Heat of reaction
  - Heats of formation of feeds and products
  - Kinetics
- Define potential for undesired reactions, decompositions
  - Effects of contaminants
  - Effects of discharging, wrong order, wrong amount
  - Effects of loss of mixing, loss of cooling
- Screen chemicals based on desired and undesired heats of reaction and reactivity
- If potential for runaway reaction or decomposition indicated
  - Review data from Reactive Chemistry Lab
  - Carry out more sensitive evaluations
  - Develop reaction models for Reactive Chemistry Lab testing

Review compatibility problems from accidental mixing

PREPARE MATRIX OF ALL POSSIBLE CHEMICALS

H	F	R		Dimethyl Chickenwire	Sat. Chickenwire	Polychickenwire	Widgetane	Sawdust	Stainless Steel
3	3	2	Dimethyl Chickenwire						
2	2	2	Sat. Chickenwire	a0					
1	1	0	Polychickenwire	a0	a0				
1	3	2	Widgetane	b3	a2	b1			
0	1	0	Sawdust	c2	a2	a0	a0		
0	0	0	Stainless Steel	a2	c1	a0	a0	b0	

Legend:

H = Health
F = Flammability
R = Reactivity

4 = Extreme Danger
3= Severe Danger
2= Danger
1= Caution
0 = Minimal

a = Reactive Chemical Lab test
b = Expert Opinion
c = Published Literature

Advantages of the Reactive Chemistry Methodology

- Expands process understanding
  - Insights into transient phenomena
  - Process behavior outside normal temperature/pressure envelope
- Uses specialized equipment
  - Designed to be safe at elevated pressures/temperatures
  - Small, relatively cheaper to run
    - Micro-reactors compared to autoclaves
    - Modular approach
    - Designed for relatively easy “what-if” studies
  - Measures heat release
  - Experiments can be designed to obtain reaction kinetics
- Produces information for safe reactor design, operating guidelines and hazard mitigation
  - Improved operating procedures
  - Cost effective design
  - Avoidance of personnel injury and equipment damage
  - Minimum production loss
  - Reduced shutdowns due to premature catalyst deactivation

Reactive Chemistry Facilities

ARC REACTIVE CHEMISTRY UNIT

PHI-TEC REACTIVE CHEMISTRY UNIT

Other units not shown
- Differential Scanning Calorimeter (DSC)
- RC1 (Isothermal Calorimeter)

APPLYING INHERENT SAFETY AND REACTIVE CHEMISTRY TESTING - AN EXAMPLE

- Developed new process for a product new to ExxonMobil
- Initial design concept was a "stirred pot" reactor
- Extensive reactive chemistry testing done on reactants, including mixtures of varying concentrations
- Reactor modeling revealed:
  - "stirred pot" reactor would be prone to quick, hard to control runaway reactions for various upset conditions
  - Tubular "pumparound" reactor was much more "forgiving" (slower to run away during upsets and easier to control)
- After extensive pilot plant testing, tubular pumparound reactor was chosen for the commercial plant. Has performed well for over five years with no reactor runaway incidents.

CHEMICALS HAZARD MANAGEMENT AT EXXONMOBIL -- SUMMARY

- Addressed comprehensively in all facets of ongoing operations and capital projects
- Reliance on Inherent SHE principles
  - Reduce or eliminate hazards
  - Minimize need for safety critical equipment and procedures
- Well-defined ISHE Review Process in place
  - Have been successful in addressing key areas of Intensify, Substitute, Attenuate and Simplify
- Strong awareness of need to recognize and understand reactive chemistry issues
  - Reactive Chemistry Laboratory plays major role in design of safe equipment and operating procedures